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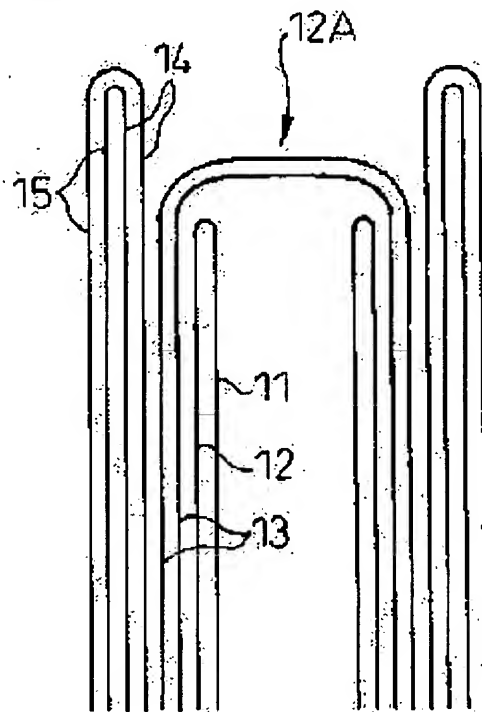
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### (54) FINE CARBON FIBER AND METHOD FOR PRODUCING THE SAME

#### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a fine carbon fiber having good electrical conductivity, having an outer diameter of <400 nm, especially of 2-300 nm, and used as a filler material with good adhesion to a resin or the like, and to provide a method for producing the fine carbon fiber, capable of producing the carbon fiber in a mass production scale, and capable of giving an field electron-emitting material chemically and thermally stable, excellent in electron emission characteristics, and having a long lifetime.

**SOLUTION:** This fine carbon fiber has a multiple-layer structure in which cylindrical carbon sheets overlap each other, a center axis of which has a hollow structure, an outer diameter of 2-30 nm, and an aspect ratio of 10-15,000, wherein at least one layer of the cylindrical carbon sheet is turned at the end of the carbon fiber to be continuous with another cylindrical carbon sheet among the multiple layers, so that the turned and continuous cylindrical carbon sheet forms a cylinder of which the end opens.



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**CLAIMS**

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[Claim(s)]

[Claim 1] The detailed carbon fiber characterized by the cylinder-like carbon sheet forming the cylinder structure where are the detailed carbon fiber which it is nothing, and the medial axis is hollow structure, and are the outer diameter of 2-300nm, and aspect ratios 10-15000, and the cylindrical carbon sheet of at least one layer turns up overlap multilayer structure between said multilayers in the point of this carbon fiber, and the cylindrical carbon sheet which turns up and continues is opening it by the point continuously with another cylindrical carbon sheet.

[Claim 2] The detailed carbon fiber according to claim 1 to which it turns up and a continuous cylindrical carbon sheet is characterized by existing in the periphery section of multilayer structure.

[Claim 3] The detailed carbon fiber according to claim 2 characterized by the cylindrical carbon sheet which the point has closed existing inside the cylinder structure which is turned up and a continuous cylindrical carbon sheet forms.

[Claim 4] The detailed carbon fiber according to claim 3 characterized by the cylindrical carbon sheet which constitutes the shape of a cylinder which turned up by the point inside the cylindrical carbon sheet which the point closed, and was further opened by the point of a carbon fiber in succession [ each other ] to it existing.

[Claim 5] The detailed carbon fiber characterized by a detailed carbon fiber according to claim 1 to 4 occupying more than 5 mass % in the outer diameter of 2-300nm, and the detailed carbon fiber of aspect ratios 10-15000.

[Claim 6] The detailed carbon fiber according to claim 5 to which a detailed carbon fiber is characterized by occupying 5 - 90 mass % into the outer diameter of 2-300nm, and the detailed carbon fiber of aspect ratios 10-15000.

[Claim 7] The detailed carbon fiber to which the detailed carbon fiber according to claim 1 to 6 observed with a transmission electron microscope in the outer diameter of 2-300nm and the detailed carbon fiber of aspect ratios 10-15000 is characterized by occupying 3 - 80 volume %.

[Claim 8] The detailed carbon fiber according to claim 1 to 7 characterized by a detailed carbon fiber being a gaseous-phase method carbon fiber.

[Claim 9] The detailed carbon fiber according to claim 1 to 8 characterized by containing a boron element in a carbon fiber.

[Claim 10] The detailed carbon fiber according to claim 1 to 9 characterized by a boron element permuting a part by the carbon element of a carbon fiber.

[Claim 11] The outer diameter of 2-300nm whose tubed carbon sheet is nothing and the medial axis of whose is hollow structure about overlap multilayer structure, the method of manufacturing a detailed carbon fiber according to claim 1 to 10 by heat-treating the detailed carbon fiber of aspect ratios 10-15000.

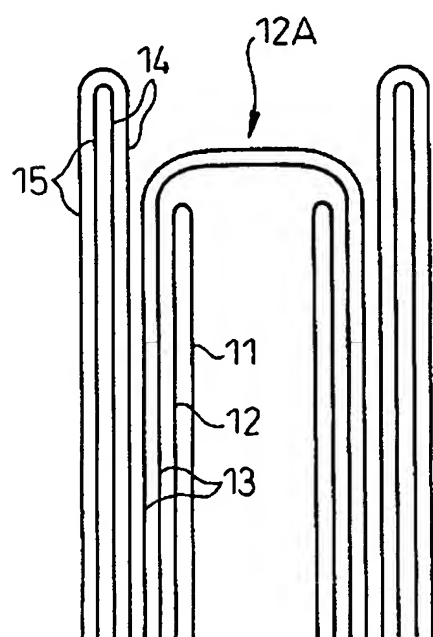
[Claim 12] The manufacture approach of the detailed carbon fiber according to claim 11 characterized by heat treatment temperature being 2000 degrees C - 3500 degrees C.

[Claim 13] The manufacture approach of the detailed carbon fiber according to claim 11 or 12

characterized by mixing and heat-treating the outer diameter of 2-300nm, and the detailed carbon fiber and boron compound of aspect ratios 10-15000 whose tubed carbon sheet is nothing, and the medial axis of whose is hollow structure about overlap multilayer structure.

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[Translation done.]

Drawing selection Representative drawing ☒

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the detailed carbon fiber for which it was especially suitable as the filler, the semiconductor material, catalyst, or field-electron-emission ingredient of composites, such as resin and rubber, and its process about the detailed carbon fiber with unique structure, process, and application.

[0002]

[Description of the Prior Art] The carbon fiber is used for various kinds of composite material from the outstanding properties, such as the high intensity, a rate of high elasticity, and high conductivity. Taking advantage of the conductivity with which not only a mechanical property but the outstanding carbon fiber or outstanding carbon material applied from the former was equipped, the application as the conductive resin filler for an electromagnetic shielding material and electrostatic prevention material or a filler for electrostatic coating to resin has been expected with development of an electronics technique in recent years. Moreover, taking advantage of the description of the chemical stability as a carbon material, thermal stability, and the fine structure, the application as field-electron-emission ingredients, such as a flat display, is expected.

[0003] The conventional carbon fiber is produced as the so-called organic system carbon fiber manufactured by heat-treating fiber, such as PAN, a pitch, and a cellulose, and carbonizing. It is desirable in order that making a path thin in order to enlarge a touch area with a base material, when using these as a filler of fiber strengthening composite, lengthening die length, etc. may raise the reinforcement effectiveness. Moreover, in order to improve an adhesive property with a base material, it is ruined to some extent, and it is [ direction ] desirable, for this reason the front face of a carbon fiber is not smooth and surface treatment, such as \*\*\*\*\*, is performed [ in air expose to an elevated temperature, and it is oxidized or ] on the front face in coating.

[0004] However, the yarn diameter of the organic fiber from which these carbon fibers serve as the raw material was about 5-10 micrometers, and was impossible for the manufacture of a carbon fiber with a small path. Moreover, a limitation is in the ratio (aspect ratio) of die length to a path, and the carbon fiber with an aspect ratio it is thin and large was demanded.

[0005] Moreover, about use of the resin to the automobile body, or use of the resin, rubber, etc. to electronic equipment, about the same conductivity as a metal was required, and in connection with this, in order that the carbon fiber as filler material might also fill the demand of these various conductive paints, conductive resin, etc., the need of raising conductivity came out. It is usually that it is necessary to raise these properties by graphitizing as a means for that, for this reason graphitization processing further in an elevated temperature is performed. However, in order not to be obtained but to compensate this, when loadings were made [ many ], the problem that workability and a mechanical property fell produced about the same conductivity as a metal, and improvement in the reinforcement by the further conductive amelioration of fiber itself and narrow-diameter-izing of fiber etc. has been needed by this graphitization processing. moreover -- as a field-electron-emission ingredient -- the former -- Spindt --

although research and development in the field electron emission by law had been done, many processes were required for the process, and although the tip was processed into the electron emission section needlelike and was conventionally used for it using Mo etc., when it used as an electron emission ingredient of a display, it was thermally [ chemically and ] inadequate.

[0006] Then, a gaseous-phase method carbon fiber (Vapor Grown Carbon Fiber; it omits Following VGCF.) came to be studied late in the 1980s as what completely differs in these organic system fiber and a process. When this VGCF carries out gaseous-phase pyrolysis of the gas, such as a hydrocarbon, under existence of an organic transition-metals system catalyst, it is known that the diameter of 1 micrometer or less and the carbon fiber to several 100nm will be obtained. For example, organic compounds, such as benzene, are used as a raw material, organotransition metal compounds, such as a ferrocene as a catalyst, are introduced into a hot fission reactor with carrier gas, and the approach (JP,60-27700,A) of making it generate on a base, the method (JP,60-54998,A) of making VGCF generate in the state of suspension, or the method (JP,2778434,B) of making it grow up to be a fission reactor wall is indicated.

[0007] According to these processes, it is comparatively thin, and excels in conductivity, and the carbon fiber suitable for the large filler material of an aspect ratio came to be obtained, and with an about 100-200nm diameter, an about ten to 500-aspect ratio thing is fertilized, and it came to be used for the filler for resin, the add-in material of a lead accumulator, etc. as conductive filler material.

[0008] These VGCF(s) are fiber which the description is in a configuration or the crystal structure, shows the structure which the crystal of a carbon hex-steel side was wound around the cylindrical shape in the shape of annual rings, and carried out the laminating, and has a very thin centrum in the core. However, about these VGCF(s), the thing of a less than 100nm still thinner diameter was not able to be manufactured on a scale of mass production.

[0009] Moreover, the multilayer carbon nanotube was discovered by Iijima and others by arc discharge in gaseous helium as a carbon fiber still thinner than this VGCF out of the soot which evaporated the carbon electrode. It is 1nm - 30nm, and the crystal of a carbon hex-steel side laps several times over in the shape of annual rings centering on the shaft of fiber like VGCF, and the diameter of this multilayer carbon nanotube is closed in the shape of a cylinder, and is a detailed carbon fiber which has a diameter of hollow in that core.

[0010] About the approach of using this arc discharge, it is not fit for mass production from that process, and has not resulted in utilization.

[0011] On the other hand, some which are depended on a gaseous-phase method have a big aspect ratio and the possibility of high conductivity, this approach is improved, and the attempt which is going to manufacture a thinner carbon fiber is made. In U.S. Pat. No. 4663230 and JP,3-64606,B, the carbon fibril of the shape of a cylinder which consists of 100 or more-aspect ratio graphite with an about 3.5-70nm diameter is indicated. The continuation layer of the carbon atom arranged regularly is arranged in the said alignment to a cylinder shaft over a multilayer, C shaft of each class of a carbon atom lies at right angles to the cylinder shaft of fibril substantially, and the structure has a smooth front face excluding the heat carbon coat which deposits by the pyrolysis in the whole.

[0012] Similarly, the carbon fiber by the gaseous-phase method of aspect ratios 2-30000 is introduced to JP,61-70014,A by 10-500nm, and it is describing at it that the thickness of a pyrolytic carbon layer is 20% or less of a diameter.

[0013] Since the front face is smooth, each of these above-mentioned carbon fibers is lacking in an adhesive property, wettability, and compatibility, and in using as a composite material, the surface treatment of oxidizing a front face enough is needed. Moreover, to use as a field-electron-emission ingredient, it is necessary to make a tip thin.

[0014]

[Problem(s) to be Solved by the Invention] In this invention, it is the purposes conductive good less than 400nm, to obtain the adhesive good detailed carbon fiber to resin etc. on a scale of mass production as 2-300nm filler material especially, and for it to be thermally [ chemically and ] stable, to excel in the electronic emission characteristic, and to obtain the long field-electron-emission ingredient of a life.

[0015]

[Means for Solving the Problem] this invention persons developed the process of VGCF from the former, and a new detailed carbon fiber with the structure different from the former and its manufacture approach were completed. Namely, about overlap multilayer structure, a (1) cylinder-like carbon sheet is nothing and the medial axis is hollow structure. Are the detailed carbon fiber which are the outer diameter of 2-300nm, and aspect ratios 10-15000, and in the point of this carbon fiber, the cylindrical carbon sheet of at least one layer turns up between said multilayers, and another cylindrical carbon sheet is followed. The detailed carbon fiber to which the cylindrical carbon sheet which turns up and continues is characterized by forming the cylinder structure currently opened by the point.

(2) A detailed carbon fiber given in (1) to which it turns up and a continuous cylindrical carbon sheet is characterized by existing in the periphery section of multilayer structure.

(3) A detailed carbon fiber given in (2) characterized by the cylindrical carbon sheet which the point has closed existing inside the cylinder structure which is turned up and a continuous cylindrical carbon sheet forms.

(4) A detailed carbon fiber given in (3) characterized by the cylindrical carbon sheet which constitutes the shape of a cylinder which turned up by the point inside the cylindrical carbon sheet which the point closed, and was further opened by the point of a carbon fiber in succession [ each other ] to it existing.

(5) The detailed carbon fiber characterized by a detailed carbon fiber given in (1) - (4) occupying more than 5 mass % in the outer diameter of 2-300nm, and the detailed carbon fiber of aspect ratios 10-15000.

(6) A detailed carbon fiber given in (5) to which a detailed carbon fiber is characterized by occupying 5 - 90 mass % into the outer diameter of 2-300nm, and the detailed carbon fiber of aspect ratios 10-15000.

(7) The detailed carbon fiber to which the detailed carbon fiber given in (1) - (6) observed with a transmission electron microscope in the outer diameter of 2-300nm and the detailed carbon fiber of aspect ratios 10-15000 is characterized by occupying 3 - 80 volume %.

(8) The detailed carbon fiber given in (1) - (7) characterized by a detailed carbon fiber being a gaseous-phase method carbon fiber.

(9) A detailed carbon fiber given in (1) - (8) characterized by containing a boron element in a carbon fiber.

(10) A detailed carbon fiber given in (1) - (9) characterized by a boron element permuting a part by the carbon element of a carbon fiber.

(11) The outer diameter of 2-300nm whose tubed carbon sheet is nothing and the medial axis of whose is hollow structure about overlap multilayer structure, the method of manufacturing the detailed carbon fiber of a publication to (1) - (10) by heat-treating the detailed carbon fiber of aspect ratios 10-15000.

(12) The manufacture approach of a detailed carbon fiber given in (11) characterized by heat treatment temperature being 2000 degrees C - 3500 degrees C.

(13) (11) characterized by mixing and heat-treating the outer diameter of 2-300nm, and the detailed carbon fiber and boron compound of aspect ratios 10-15000 whose tubed carbon sheet is nothing, and the medial axis of whose is hollow structure about overlap multilayer structure, or the manufacture approach of a detailed carbon fiber given in (12).

[0016]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. In order to obtain the outer diameter of less than 400nm with sufficient conductivity, and the detailed carbon fiber with a sufficient adhesive property to resin etc. especially as filler material (2-300nm and further 1-80nm), this invention When carrying out elevated-temperature heat treatment of the detailed VGCF under existence of a boron compound and attaining graphitization, while advancing examination, The detailed carbon fiber of the gestalt which is not known conventionally is obtained, conductivity is high, and is excellent also in the adhesive property to resin etc., it is [ this is thermally / still more chemically and / stable, and ] excellent in the electronic emission characteristic, and the long field-electron-emission ingredient of a life is given, Moreover, the detailed carbon fiber of this new gestalt finds out that heat treatment is



also that to which it is obtained not only in the bottom of existence of a boron compound, and sells. It is understood that the detailed carbon fiber of this invention is more detailed fundamentally, and is a carbon fiber of one gestalt acquired by the process in which it is going to manufacture a carbon fiber with a more high degree of graphitization. The detailed carbon fiber of this invention is explained. The description of the detailed carbon fiber of this invention is explained using an accompanying drawing ( drawing 1 -4). In these drawings, a carbon sheet (layer of the crystal near a graphite or a graphite) is typically expressed with a continuous line. The cylinder-like carbon sheet has closed the cylindrical carbon sheet with which such a well-known detailed carbon fiber constitutes multilayer structure from a point of fiber with curvature with all, although that the medial axis of whose of conventional less than 100nm and the detailed carbon fiber of aspect ratios 10-15000 are nothing and is hollow structure about overlap multilayer structure (annual-rings structure) as shown in the type section Fig. of drawing 1 is known first. On the other hand, the detailed carbon fiber of this invention has the structure like the following.

- 1) In the detailed carbon fiber 10 which a cylinder-like carbon sheet is nothing, and the medial axis is hollow structure about overlap multilayer structure, and are the outer diameter of 2-300nm, and aspect ratios 10-15000 as shown in drawing 2 and drawing 4 In the point of this carbon fiber, the cylindrical carbon sheet 14 (14a, 14b) of at least one layer turns up between said multilayers, and another cylindrical carbon sheet 15 (15a, 15b) is followed. The cylinder which the cylindrical carbon sheets 14 and 15 which turn up and continue constitute is a detailed carbon fiber characterized by being open by the point of a carbon fiber. if the conventional detailed carbon fiber is oxidized, the tip of fiber will be destroyed compulsorily -- it is (U.S. Pat. No. 5,641,466 specification) -- since it is not graphite formation conditions in that case, a carbon sheet turns up and does not continue
- 2) The detailed carbon fiber which will be characterized by said cylindrical carbon sheets 14 and 15 which turn up and continue existing in the periphery section of multilayer structure in the detailed carbon fiber of the above 1 if drawing 2 is referred to. It turns up and, generally a continuous carbon sheet is easy to be formed in the periphery section of multilayer structure.
- 3) The detailed carbon fiber which will be characterized by the cylindrical carbon sheet 13 (13a, 13b) which point 12A has closed inside the cylinder which said cylindrical carbon sheets 14 and 15 which turn up and continue form existing in the detailed carbon fiber of the above 2 if drawing 2 is referred to. Although the cylinder which is turned up and a continuous carbon sheet generally constitutes tends to exist in the periphery section of multilayer structure, the cylindrical carbon sheet existed in the inside further, and the point 12A is closed in many cases.
- 4) The detailed carbon fiber which will be further characterized by the cylindrical carbon sheets 11 and 12 which constitute the shape of a cylinder which turned up by the point and was opened by the point of a carbon fiber in succession [ each other ] existing in the detailed carbon fiber of the above 3 inside the cylindrical carbon sheet 13 which said point closed if drawing 3 is referred to.
- 5) If drawing 4 is referred to, a detailed carbon fiber will consist only of a cylinder which the carbon sheet which turns up and continues constitutes, and the thing of an open gestalt will also obtain and deal in the tip of a carbon fiber. In the cylinder which the carbon sheets 14 and 15 which turn up not only the case of drawing 4 but a detailed carbon fiber, and continue constitute, the carbon sheet 16 which is not turned up to somewhere in the interior may exist.
- 6) the inside of the outer diameter of 2-300nm, and the detailed carbon fiber of aspect ratios 10-15000 -- the above -- the detailed carbon fiber to which the detailed carbon fiber of a publication occupies more than 5 mass % one to 5 either.

As mentioned above, although the typical gestalt of the detailed carbon fiber of this invention was explained, in the point of a carbon fiber, the cylindrical carbon sheet of at least one layer turns up the detailed carbon fiber of this invention between multilayers, it is characterized by opening another cylindrical carbon sheet and the cylinder which the cylindrical carbon sheet which turns up and continues constitutes continuously by the point of a carbon fiber, and other change is arbitrary. For example, that what is necessary is just at least one layer, the adjoining cylindrical carbon sheet of two-layer or three layers or more may turn up the number of layers of the cylindrical carbon sheet which

turns up between multilayers in the point of a carbon fiber, and follows another cylindrical carbon sheet, and it may be following another cylindrical carbon sheet. Moreover, it turns up, and even if continuous cylindrical carbon sheets adjoin, they do not need to adjoin. For example, although the cylindrical carbon sheet 14 and the cylindrical carbon sheet 15 turn up and continue in drawing 4, the cylindrical carbon sheet 16 intervenes in between, and the cylindrical carbon sheet 14 and the cylindrical carbon sheet 15 do not adjoin mutually. Moreover, even if indeterminate form carbon exists in the point and perimeter of a carbon fiber which are constituted with a carbon sheet, the detailed carbon fiber of this invention is not influenced.

[0017] The detailed carbon fiber of this invention is the multilayer structure which the tubed carbon sheet which consists of a carbon atom overlapped as structure of the fiber part of detailed carbon, and a cavernous part in the air exists in a medial axis. Although these carbon sheets overlap the grain direction in the shape of a straight line in general multiplex if this is observed [ the thing which the carbon atom arranged regularly followed, or / of fiber ] from a longitudinal right angle, there is a part from which a tubed sheet breaks off in a longitudinal direction, and has become discontinuity, and the bore of the centrum of a medial axis does not need to be fixed. The above gestalten of the detailed carbon fiber of this invention are not reported by the carbon fiber by the various conventional gaseous-phase methods, but are new.

[0018] It has the different description it is featureless to the former at a tip, and the part to which the tip became thin further to the conventional carbon fiber can exist, the conductive matter with a thin tip can have the directivity of electron emission, the detailed carbon fiber of these this inventions can centralize impression electric field, and its field-electron-emission property improves, and it is suitable as a field-electron-emission component. Moreover, since the point is carrying out the anomaly similarly, when it is used as a conductive filler etc., it is effective in the adhesive property to resin etc. improving. Moreover, about this detailed carbon fiber, more than 5 mass %, ten to 70 mass %, and especially when 10 - 50 mass % was included, and a field-electron-emission property improves and it is used as a conductive filler etc. according to the description of the structure, there are further five to 90 mass % and effectiveness that the adhesive property to resin etc. improves, preferably. Moreover, although the structure of a detailed carbon fiber can be checked by observation by the transmission electron microscope, five to 70 volume %, and when are 10-50 volume % Contained preferably, and a field-electron-emission property improves and it is used as a conductive filler etc., the effectiveness that the adhesive property to resin etc. improves is in a 3 - 80 volume % pan about the detailed carbon fiber of this invention.

[0019] An outer diameter is 2-300nm, since the detailed and long fiber of aspect ratios 10-15000 is obtained, it can add so much as filler material, and the detailed carbon fiber of this invention is excellent in the reinforcement effectiveness.

[0020] Furthermore, it does not often change the complementation of ion to the conventional gaseous-phase method carbon fiber about conductivity, and since what has the above-mentioned structure does not have the smooth front face, also as for wettability with the electrolytic solution of a cell, it is good, when it is used as add-in material of a cell, since the end face of a carbon sheet had come outside. Therefore, it has the description that it is suitable as add-in material for cells. If the detailed carbon fiber which has the unique gestalt of this invention is a detailed carbon fiber and is the approach of manufacturing the high thing of graphitization, it may be manufactured, but in order to manufacture the detailed carbon fiber of this invention below, it explains a suitable approach. Generally, by pyrolyzing an organic compound, especially hydrocarbons using a transition metal catalyst, the detailed carbon fiber of this invention obtains a rough detailed carbon fiber, and it is obtained by performing 2500-3500-degree C heat treatment preferably further 2000-3500 degrees C. Since the reason a detailed carbon fiber has the above-mentioned clinch structure is considered because the distance between carbon sheets becomes small, the detailed carbon fiber of this invention is more easily obtained by adopting conditions which make carbon sheet spacing small as much as possible. Therefore, in case a rough detailed carbon fiber is heat-treated, it is advantageous to make a boron compound exist. If a boron compound is made to live together, hundreds of degrees C heat treatment temperature can be made low compared with

additive-free, and the ratio of the periphery part to the diameter of fiber can be enlarged compared with additive-free in the same heat treatment temperature. A gas is [ that what is necessary is just the matter which generates boron with heating as a boron compound ] sufficient at solid-states, such as boron carbide, a boron oxide, and an organic boron oxide, a liquid, and a gas.

[0021] A rough detailed carbon fiber is obtained by using a transition metal catalyst first and pyrolyzing an organic compound, especially hydrocarbons. An organotransition metal compound contains the transition metals used as a catalyst. as transition metals -- the [ periodic table ] -- it is an organic compound containing the metal of IVa, Va, VIa, VIIa, and a VIII group. Compounds, such as a ferrocene and NIKKERUSEN, are desirable especially. as the content of the organotransition metal compound as a catalyst -- the carbon content of an organic compound -- receiving -- 0.01 to 15.0 mass % -- desirable -- 0.03 to 10.0 mass % -- 0.1 - 5.0 mass % is preferably good. Moreover, in addition to this, although a sulfur compound is used as a co-catalyst, the gestalt does not exist and is easy to dissolve especially a limit in the organic compound which is a carbon source. As the sulfur compound, a thiophene, various thiols or inorganic sulfur, etc. is used. the amount used -- an organic compound -- receiving -- 0.01 to 10.0 mass % -- desirable -- 0.03 to 5.0 mass % -- 0.1 - 4.0 mass % is still more preferably good.

[0022] Gas and those mixture, such as CO or natural gas and methane, such as benzene, toluene, a xylene, a methanol, ethanol, naphthalene, a phenanthrene, a cyclopropane, cyclopentene, a cyclohexane organic compound, and volatile oil, kerosene, ethane, ethylene, and acetylene, are also possible for the organic compound used as the raw material of a carbon fiber. Especially aromatic compounds, such as, benzene, toluene, and a xylene, are desirable especially.

[0023] As carrier gas, the gas of reducibility including hydrogen gas is usually used. It is desirable to heat carrier gas at 500-1300 degrees C beforehand. The reason to heat is because a more detailed carbon fiber is obtained as supply of the carbon source by generation of the metal of a catalyst and the pyrolysis of a carbon compound is made in agreement with reaction time and a reaction is caused in an instant. When carrier gas is mixed with a raw material, if the pyrolysis of the carbon compound of a raw material cannot happen easily and whenever [ stoving temperature / of carrier gas ] surpasses 1300 degrees C at less than 500 degrees C, growth of the direction of a path of a carbon fiber will take place, and a path will tend to become thick.

[0024] The 1-70-mol section is suitable for the amount of the carrier gas used to the 1.0 mol section of organic compounds which is a carbon source. The path of a carbon fiber is controllable by changing the ratio of a carbon source and carrier gas. A raw material dissolves and adjusts a transition-metals compound and the sulfur compound of a co-catalyst to the organic compound of a carbon source. And although it can spray by carrier gas with a liquid and a fission reactor can also be supplied, a raw material makes a part of carrier gas evaporate as purge gas, can be supplied to a fission reactor and can also be made to react. It is more desirable to have evaporated the raw material and to supply a fission reactor, when obtaining the thin carbon fiber of the diameter of fiber.

[0025] The electric furnace of a vertical mold is usually used for a fission reactor. 800-1300 degrees C of fission reactor temperature are 1000-1300 degrees C preferably. Supply the material gas and carrier gas which made raw material liquid, carrier gas, or a raw material evaporate, they are made to react to the fission reactor which carried out the temperature up to predetermined temperature, and a carbon fiber is obtained.

[0026] Thus, the gas blown into the fission reactor pyrolyzes, an organic compound serves as a carbon source, an organotransition metal compound serves as a transition-metals particle of a catalyst, and generation of the detailed carbon fiber which used this transition-metals particle as the nucleus is performed. Further, by inert gas ambient atmosphere-ization of helium, an argon, etc., 900-1500-degree C heat treatment is performed, further 2000-3500-degree C heat treatment is performed, or 2000-3500-degree C heat treatment is performed for the detailed carbon fiber in the condition of having been obtained by the reaction, the formation of an inert gas ambient atmosphere, and directly, and the obtained detailed carbon fiber can obtain the unique detailed carbon fiber of this invention. However, after performing 900-1500-degree C heat treatment under an inert gas ambient atmosphere, the detailed

carbon in the condition of having been obtained by the reaction, or its detailed carbon fiber By mixing with boron compounds, such as boron carbide (B<sub>4</sub>C), boron oxide (B<sub>2</sub>O<sub>3</sub>), element-like boron, a boric acid (H<sub>3</sub>BO<sub>3</sub>), and a borate, and heat-treating at 2000-3500 degrees C under an inert gas ambient atmosphere further It is possible to obtain the unique detailed carbon fiber of this invention more easily. the case where boron carbide (B<sub>4</sub>C) is used, for example although it was not limited in order to depend for the addition of a boron compound on the chemical property of the boron compound to be used, and a physical characteristic -- a detailed carbon fiber -- receiving -- 0.05 to 10 mass % -- the range of 0.1 - 5 mass % is preferably good. A part of boron dissolves that boron is contained in a detailed carbon fiber, it exists between the layered product layers of the front face of a carbon fiber, and a carbon hex-steel side, and in a centrum, or the condition that a part of carbon atom and boron atom permuted is said.

[0027]

[Example] Hereafter, the example of this invention is given and explained. The feeding tubing 4 which supplies the raw material which the crowning of the vertical mold heating furnace 1 (the bore of 170mm, die length of 1500mm) was made to evaporate through the raw material carburetor 5 as shown in drawing 5 of a schematic diagram, and the carrier gas charging line 6 were attached. Ferrocene 3 mass % and the toluene of which the thiophene 1 mass % dissolution was done were made to evaporate, and it supplied by part for 20g/, and was made to supply and react by part for 75l./from the feeding tubing 4, using hydrogen as carrier gas. The transmission electron microscope photograph of the detailed carbon fiber obtained at this reaction is shown in drawing 6. The detailed carbon fiber obtained at this reaction was heat-treated at 1300 degrees C under Ar (argon) ambient atmosphere, 1300 more degree-C processing article was heat-treated at 2800 degrees C under Ar ambient atmosphere, and the detailed carbon fiber was obtained at 96% of weight recovery. Moreover, 4 mass % mixing of B<sub>4</sub>C was done to the bottom 1300-degree-C heat treatment article of Ar ambient atmosphere of this detailed carbon fiber, it heat-treated at 2800 degrees C under Ar ambient atmosphere, and the detailed carbon fiber was obtained at 94% of weight recovery. This transmission electron microscope photograph is shown in drawing 7. It is the multilayer structure which the tubed carbon sheet with which drawing 6 and drawing 7 consist of a carbon atom overlapped, and the medial axis is hollow structure. However, although it corresponded to the mimetic diagram of drawing 1 and the tip has closed in drawing 6, the multilayer structure which has a gestalt corresponding to the mimetic diagram of drawing 3 about is seen in drawing 7. That is, in drawing 7, it has the periphery section (it corresponds to 14 of drawing 3, and 15) which forms the cylinder which the tip opened, the pars intermedia (it corresponds to 13 of drawing 3) which the tip closed, and the cylinder (it corresponds to 11 of drawing 3, and 12) which the tip opened to the inside further. Moreover, the end of each carbon sheet (it corresponds to 14, 15 and 11 of drawing 3, and 12) which constitutes the outside and the inside of multilayer structure is turning up, joining together and following each other. The tip (it corresponds to 12A of drawing 3) has closed the carbon sheet (it corresponds to 13 of drawing 3) which makes the middle of the layer of the carbon sheet which the outside of multilayer structure and the inside turned up. In addition, in drawing 7, although a carbon sheet appears in the direction of a cross section of fiber in the point of a carbon fiber, this carbon sheet cannot have the seen clinch part of the carbon sheet of the periphery section as a carbon sheet, and a carbon sheet does not necessarily exist in the axial center section of fiber. Moreover, although the point of the carbon sheet of the point which the pars intermedia carbon sheet closed is not a cavity in the point of a carbon fiber and it seems similarly that some matter exists, indeterminate form carbon has not adhered and this part is not related to the structure of a carbon fiber. It is found that indeterminate form carbon exists also in the periphery section front face of a carbon fiber.

[0028] As for the outer diameter of the fiber at this time, ten or more aspect ratio numbers fiber was produced by about 10-100nm. Moreover, when observed with the transmission electron microscope, fiber with the above-mentioned description was more than a moiety.

[0029]

[Effect of the Invention] According to this invention, unlike the conventional carbon fiber or a gaseous-phase method carbon fiber, an outer diameter is 2-300nm. The aspect ratio by 10-15000 In the point of this carbon fiber, the cylindrical carbon sheet of at least one layer turns up between said multilayers, and

another cylindrical carbon sheet is followed. The cylindrical carbon sheet which turns up and continues can offer the detailed carbon fiber characterized by forming the cylinder currently opened by the point, and is useful as field electron emission, gaseous occlusion, and a conductive filler for resin.

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[Translation done.]